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ORIGINAL ARTICLE

Influences of pH and CO_2 on the formation of Metasilicate mineral water in Changbai Mountain, Northeast China

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Abstract Mineral dissolution reactions actively participate in controlling the composition of mineral water. In this study, water soluble, acidic–alkaline and carbonated solution experiments were designed, and mineral reaction mechanisms were researched using chemical kinetics and the minimum free-energy method. The results showed that the release of metasilicate was controlled by pH, CO_2, and rock characteristics. In the water soluble experiment, the release process of metasilicate in powdered rocks reached equilibrium after 40 days, while metasilicate in solid rocks took 170 days. The release process of metasilicate in solid rocks satisfied an asymptotic model, while in powdered rocks it accorded with the Stanford reaction kinetic model. In the acidic–alkaline experiment, metasilicate was released earlier under acidic conditions ($2.46 < pH < 7$) than under alkaline conditions ($7 < pH < 10.61$). The release process of metasilicate under acidic conditions reached equilibrium in 40 days, compared with 60 days for alkaline conditions. The addition of CO_2 to the water solution was beneficial to the formation of metasilicate. Under neutral pH conditions, the reaction barely occurred. Under alkaline conditions, metasilicate was produced by the hydrolysis of metasilicate minerals. Under acidic and additional CO_2 conditions, metasilicate formation was mainly via the reaction of H^+, CO_2, and metasilicate minerals. From these results, we concluded that the metasilicate mineral water from the Changbai Mountains, Jingyu County, is generated by a combination of the hydrolysis of metasilicate minerals and the reaction of H^+, CO_2, and metasilicate minerals. These results can contribute to a better development and protection of the mineral water resources in the Changbai Mountains.

Keywords Mineral water · Metasilicate · pH · CO_2 · Chemical kinetics analysis · Minimum free energy · Changbai Mountain

Introduction

Formation and distribution of mineral waters is under the control of active faulted structure and lava rocks commonly, and the characteristic elements mainly come from water–rock interaction (Zhang 2001; Bahri and Saibi 2012). Many studies have been conducted on chemical composition of mineral water in relation with rock materials. Most of these studies focused on mica minerals and carbonate rocks; little is known about the mechanism of metasilicate mineral dissolution in mineral water in basalt area.

Key factors influencing water–rock interaction include temperature, pH, pressure, catalysis, and rock characteristics (Gérard et al. 2002; Oelkers et al. 2008; Gysi and Stefánsson 2011; Pachana et al. 2012). Gérard et al. (2002) investigated the relationships between Si concentration, soil temperature, and H^+ concentration, and concluded that silica concentration was controlled by soil temperature and H^+ concentration. Oelkers et al. (2008) gave an overview on the steady-state muscovite dissolution rates at temperatures from 60 to 201 °C and $1 \leq pH \leq 10.3$ as a

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function of reactive solution K, Si, and Al concentration. The findings of Pachana et al. (2012) in analyzing the dissolution generates etch in the surface of biotite and muscovite basal at different pH values (pH 1.1, 3.3, and 5.7) and different temperatures ($T = 2.5$, 120, and 200 °C) were very important, as he concluded that dissolution regime changes with pH values and temperatures. Skopljak and Vlahović (2012) wrote about the genesis of mineral waters in Kiseljak surroundings, and pointed out that the water origin from atmospheric and water descends in the primary aquifer where it becomes enriched with CO_2 and minerals. The source of elements in mineral water mainly generated in the reaction with groundwater and surrounding rocks (Shen and Zhou 1987; Zhou 1992; Ai et al. 1998; Zhang et al. 1999). Shen and Zhou (1987) studied that the hydrogeochemical mechanism of mineral water was formed containing silicon by the chemical thermodynamic in Huaying mountain, and came up with the reason of soluble silica in the groundwater. Zhou (1992) studied the chemical causes of natural drinking mineral water containing silicon of Wolong, because of feldspar quartz sandstone, microcline, and albite dissolutions, containing silicon and calcium, which produced silicon and Strontium. Dang and Hou (1995) researched the dissolution mechanism of basalt in acidic and alkaline solution at closed system with normal temperature and pressure, and acknowledged that the pH value of solution eventually became neutral. Ai et al. (1998) analyzed the trend of mineral dissolution and precipitation of the interaction process of groundwater and basalt in Xuyi using the saturation index of the groundwater components by establishing water chemical equilibrium reaction model. Zhang et al. (1999) discussed the sources of soluble silicon, strontium, lithium, zinc, selenium which were mainly produced by water–rock reaction in the groundwater.

Although there are many researches about the origin of the mineral water elements, the mechanism of metasilicate mineral water in the basalt area of JingYu County and the effects of pH and CO_2 on water–rock interaction are not clear. The formation of metasilicate mineral requires about 40 years by tritium isotope (Yan et al. 2015), which is a long time for human, and the flow discharges of the springs were reducing. So detecting the formation mechanism of mineral water and making appropriate measures to protect it are crucial. Rocks of JingYu County were sampled as experimental materials. Water soluble, acidic–alkaline, carbonated solution experiments were designed, and studied the influences of pH and CO_2 on the formation mechanism of metasilicate mineral water through the simulation test in door. This paper was also completed on the basis of field investigated and the results of experiments in door.

Study area

Jingyu County, covering a total land area of 3094.4 km^2, is located in the southeast of Jilin Province, northeast China. The area is characterized by a temperate continental monsoon climate, with an annual average temperature of 3.7 °C and an annual average precipitation of 749.7 mm, much of which occurs between June and September. Mineral water is produced by 18 springs located in a 15306-ha protection zone in the Changbai Mountain (Fig. 1), southwest Jingyu. Among the 18 springs, Feilong, Jiulong, and Wulong have maximum flow discharge.

The study area is within Changbai Mountain. It is located on the basalt platform of the Quaternary Pleistocene, surrounded by the volcanic cluster of the Longgang Region, which had an olivine basalt lithology (Fig. 2). The study area is at the point where the latitudinal tectonic system and Neocathaysian structural system joint, existing east–west break (XingHua-Mount Paektu break), northwest break, and northeast break (JiAn-Songjiang lithosphere break) meet. The neotectonic movement in the region has strong drape faults that are well developed, and there are extensive basalt outcrops. The basalt varies from 120 to 15 m thick, and the degree of the fracture also declines, from the middle of the platform to the edge of the protected area, which has resulted in a reduction in the groundwater recharge capacity and the quantity of water in the aquifer. Based on the groundwater storage conditions, physical properties of water and the hydrological and hydraulic characteristics, the groundwater in the study area can be divided into pore water in loose beds, basalt pore-fissured water, and granite fissure water.

Experiments and methods

Rock materials

The test rock samples were mainly collected from Jingyu County, including Baijiang, Sihailongwan, Feilong, and Wangdashan springs as well as experimental well. The mineral compositions of rock consisted of forsterite and plagioclase, and matrix was composed of plagioclase, magnetite, and pyroxene. Table 1 shows the chemical compositions of the rocks. There are no specific permissions required for the study area (Jingyu County, Changbai Mountain), because it is just a scientific research and would help the local people. Meanwhile, the field studies did not involve endangered or protected species.

Water soluble experiment

The materials of water soluble experiment contain powdered rocks and solid rocks. Powdered rocks with particle

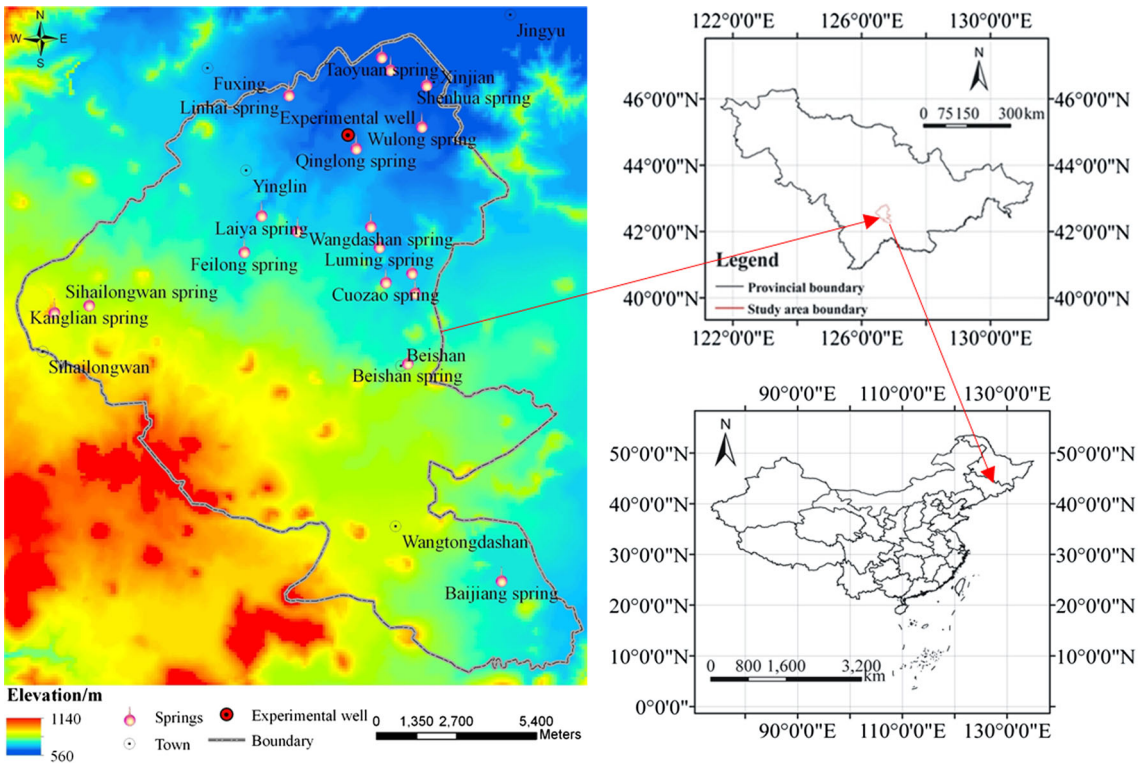

Fig. 1 The location of study area

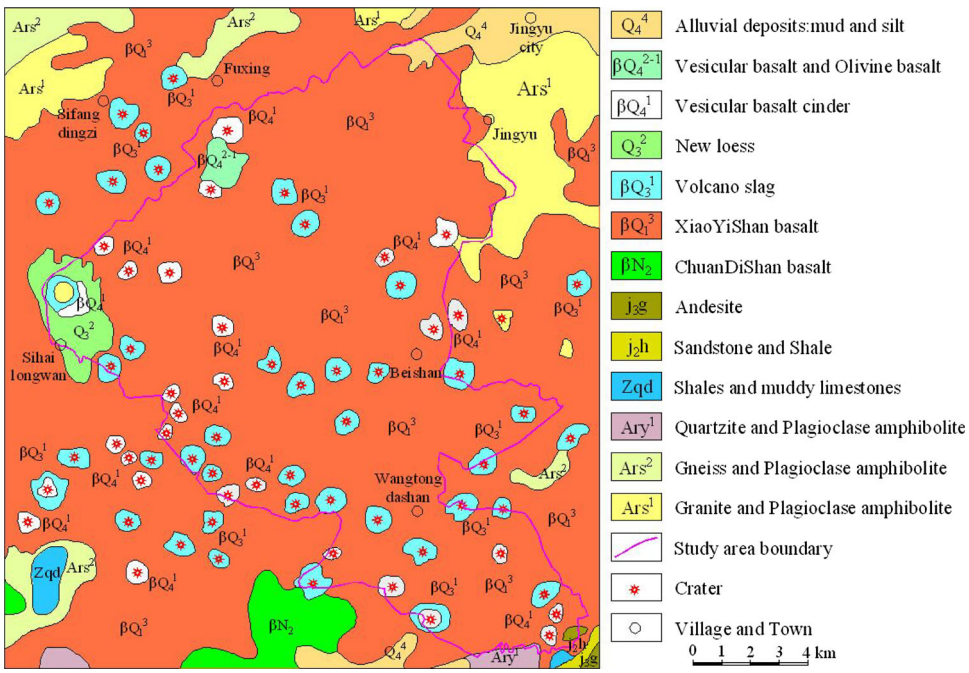

Fig. 2 Geological map of the study area

size of 200 meshes were sampled from four springs above and experimental well, while solid rocks with 1.50 × 0.35 × 1.40 cm^3 were sampled from experimental well. All of the experimental rock samples were placed into deionized water with the water–rock ratio of 5:1 in a sealed container with initial pH value of 7.1. Measurements were made daily during the first week and weekly from 2 to 30 weeks. After reaction, the solution from each container was collected using a syringe and filtered through a 0.2-μm pore-size minisart filter. Sampled solutions were divided

Table 1 Chemical composition (%) of rock samples collected from study area

Location of rock samples	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	LOI
Baijiang spring	52.96	12.82	4.76	4.91	13.71	4.04	0.77	2.83	0.88	0.12	0.06	1.57
Sihailongwan spring	50.3	19.22	4.24	6.46	6.59	2.22	2.55	4.02	2.03	0.71	0.08	1.05
Feilong spring	49.46	18.56	4.63	5.17	7.87	3.91	2.09	4.37	1.95	0.64	0.07	0.82
Wangdashan spring	48.3	19.05	10.88	2.69	5.58	2.54	2.20	3.42	2.32	0.67	0.17	1.74
Experimental well	50.04	15.79	6.25	4.7	8.25	4.21	2.07	3.73	1.95	0.46	0.15	1.81

into two aliquots: one for SiO_2 analysis and the other for pH analysis.

Acidic–alkaline experiment

The materials of acidic–alkaline experiment were powdered rocks with particle size of 200 meshes from four springs above and experimental well. All of the experimental rock samples were placed into deionized water with the water–rock ratio of 5:1 in a sealed container at varied initial pH values of 2.46 and 10.61. Measurements were made daily during the first week and weekly from 2 to 30 weeks. After reaction, the solution from each container was collected using a syringe and filtered through a 0.2-μm pore-size Minisart filter. Sampled solutions were divided into two aliquots: one for SiO_2 analysis and the other for pH analysis.

Carbonated solution experiment

The materials of acidic–alkaline experiment were powdered rocks with particle size of 200 meshes from Wangdashan spring. Rock samples were placed into deionized water with the water–rock ratio of 5:1 in a container at varied initial pH values of 3.20, 7.64, and 11.48. CO_2 was injected into the container at a rate of 0.05–0.1 m^3/min for 5 min every other day. Measurements were taken daily during the first week and weekly from 2 to 10 weeks. After reaction, the solution from each container was collected using a syringe and filtered through a 0.2-μm pore-size minisart filter. Sampled solutions were divided into two aliquots: one for SiO_2 analysis and the other for pH analysis.

Chemical kinetic analysis

Using Stanford reaction kinetic model (Stanford and Smith 1972; Zhang et al. 2012) to simulate the release process of metasilicate with powder samples of the water soluble experiment and carbonated solution experiment (initial pH acidic), cumulative release was estimated by Eq. 1.

$$M_t = M_0[1 - \exp(-k_m t)], \quad (1)$$

where M_t (mg/kg) is the metasilicate cumulative release; M_0 (mg/kg) is the potential release of metasilicate; k_m ($days^{-1}$) is release rate constant; t (days) is the reaction time.

Using asymptotic model (Knauss and Wolery 1986) to simulate the process of metasilicate with solid samples of the water soluble experiment, cumulative release was estimated by Eq. 2.

$$M_t = M_0 - k_m k_d^t, \quad (2)$$

where M_t (mg/kg) is the metasilicate cumulative release; k_m ($days^{-1}$) and k_d ($days^{-1}$) are release rate constants; t (days) is the reaction time.

Using Boltzmann reaction kinetic model (Yan and Zhang 2008; Liu and Zhou 2009) to simulate the release process of metasilicate of the carbonated solution experiment (initial pH neutral and alkaline), cumulative release was estimated by Eq. 3.

$$M_t = A_2 + \frac{(A_1 - A_2)}{\left\{1 + \exp\left[(t - A_0)/dt\right]\right\}}, \quad (3)$$

where M_t (mg/kg) is the metasilicate cumulative release; A_0, A_1, and A_2 (mg/kg) are release rate constants; t (d) is the reaction time.

Minimum free-energy method

Chemical reaction follows mass conservation principle, charge conservation principle, and electronic balance principle. The smaller the free-energy consumption, the chemical reaction is more prone. The mineral reaction linear programming model was established by the lowest energy principle and chemical thermodynamics principle using water samples information balanced of wangdashan spring of the water soluble experiment, pH alkaline experiment, and carbonated experiment (initial pH acidic). The objective function (4) is the lowest free-energy change ΔG of the chemical reactions (He et al. 2008; Liu et al. 2010; Hareeparsad et al. 2011).

$$\min X = \Delta G_{r1}X_1 + \Delta G_{r2}X_2 + \cdots\cdots + \Delta G_{rn}X_n = \sum_{i=1}^{n} \Delta G_{ri}X_i, \quad (4)$$

where X (J/L) is the free energy consumed of chemical reaction; ΔG_{ri} is the free-energy change of i chemical reaction (J/mol); X_i is the free energy consumed of i chemical reaction (mol/L); n is the total number of reactions.

Results

pH, metasilicate, and chemical kenetic process in water solution

All sample solutions showed a similar trend of pH with time (Fig. 3). In the powdered rocks, it was found that pH rose during the first 25 days, reduced afterward to day 52, and then increased again afterward and remained weak alkaline after 71 days. The pH of the solid rocks changed lag than in powdered rocks, pH increased in the first 40 days, and reduced between 40 and 63 days, and later pH tended to neutral.

All sample solutions showed a similar trend of metasilicate with an initial rise within the first 25–40 days and steady-state afterward, but at different magnitudes (Fig. 4). In the powdered rocks, it was found that the metasilicate cumulative releases increased quickly in the first 25 days of the investigation. On the reaction of 40th day, the reaction of Baijiang spring and Feilong spring reached equilibrium while others at the reaction on the 60th day. The maximum of the cumulative releases of metasilicate were different on the equilibrium solution as the samples rock varied. In the solid rocks, the cumulative release of metasilicate increased slowly, and the reaction reached equilibrium after the 160th day. The maximum of the cumulative release of metasilicate at the equilibrium reaction with solid sample was less than powdered sample.

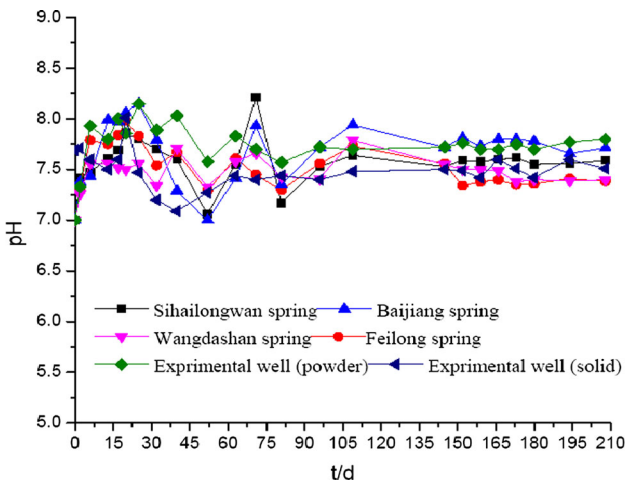

Fig. 3 The curve of pH of the water soluble experiment

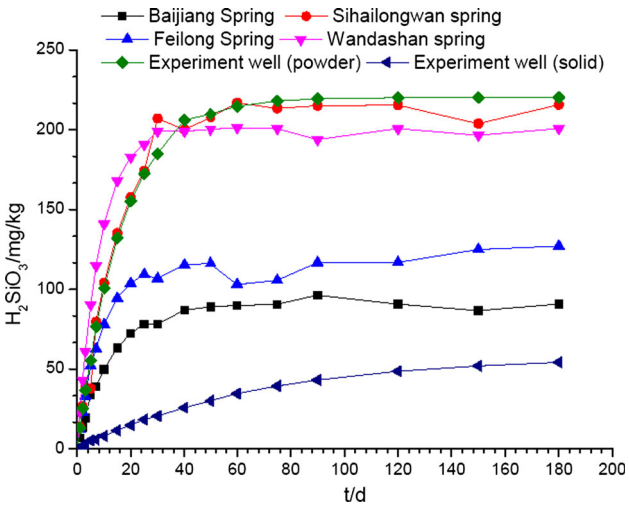

Fig. 4 The curve of H_2SiO_3 of the water soluble experiment

The release process of metasilicate of solid rocks satisfied asymptotic model while that of the powdered rocks accorded with Stanford reaction kinetic model. Equation 5 shows the asymptotic model and Table 2 shows the parameters of Stanford model.

$$M_t = 57.99 - 58 \times 0.985^t \quad (5)$$

pH and metasilicate in acidic and alkaline solutions

All sample solutions showed a similar trend of pH with time (Fig. 5). In the acidic solution, the initial pH value was 2.46, and then increased rapidly from 2.46 to above 7.00 in the first 20 days in the reaction of Baijiang spring and Feilong spring, and declined between 20 and 30 days, then increased again and tended to neutral finally (Figs. 6, 7). In the alkaline solution, the initial pH value was 10.61, and then reduced rapidly from 10.61 to about 8.00, and tended to neutral finally.

All sample solutions showed a similar trend of metasilicate with an initial rise within the first 40–60 days and steady-state afterward, but at different magnitudes (Figs. 7, 8). For Sihailongwan spring, the metasilicate cumulative releases reached maximum value (133.18 mg/kg) at 40th days in acidic experiment, while the time of maximum value (90.75 mg/kg) at 60th days in alkaline experiment.

The release process of metasilicate of the acidic–alkaline experiment complies with Stanford reaction kinetic mode. Tables 3 and 4 show the kinetic model parameters.

pH and metasilicate in carbonated solution

In carbonated solution, pH value tended to faintly acid (Fig. 9). Initial pH alkaline and neutral solutions showed a similar trend of metasilicate. Metasilicate of solution was slowly increased within 7 days, and then increased quickly

Table 2 The kinetic model parameters for metasilicate release process in the water solution experiment

Location of rock samples	M_0 (mg/kg)	k_m (days)	Fitting equation	R^2
Baijiang spring (powdered)	90.68	0.079	$M_t = 90.68[1 - \exp(-0.079t)]$	0.90
Wangdashanspring (powdered)	200.74	0.12	$M_t = 200.74[1 - \exp(-0.12t)]$	0.91
Feilong spring (powdered)	116.72	0.11	$M_t = 116.72[1 - \exp(-0.11t)]$	0.91
Sihailongwan spring (powdered)	215.61	0.066	$M_t = 215.61[1 - \exp(-0.066t)]$	0.90
Experimental well (powdered)	220.25	0.061	$M_t = 220.25[1 - \exp(-0.061t)]$	0.90

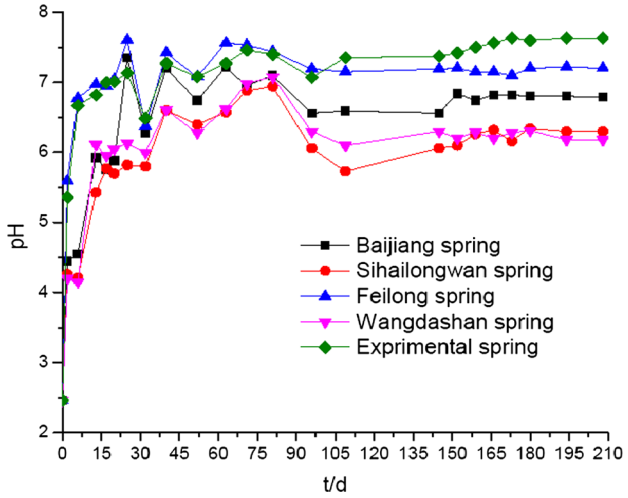

Fig. 5 The curve of pH of pH acidic experiment

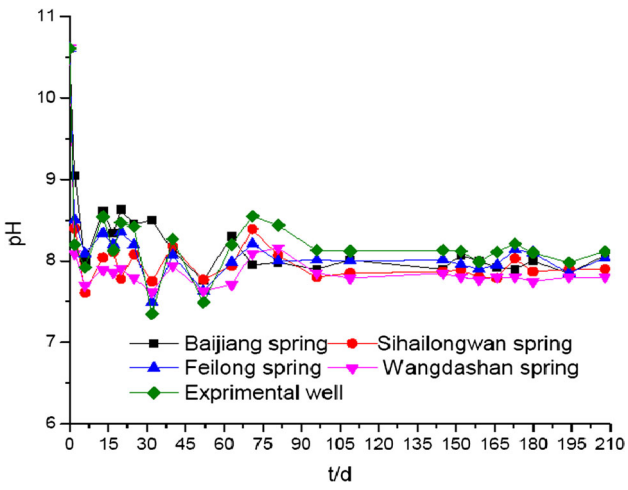

Fig. 6 The curve of pH of pH alkaline experiment

between 7 and 42 days. Metasilicate was increased quickly at beginning of reaction (Fig. 10).

The release process of metasilicate of the carbonated solution (initial pH neutral or alkaline) complied with Boltzmann reaction kinetic model (6, 7), while the initial pH acidic complied with Stanford reaction kinetic model (8).

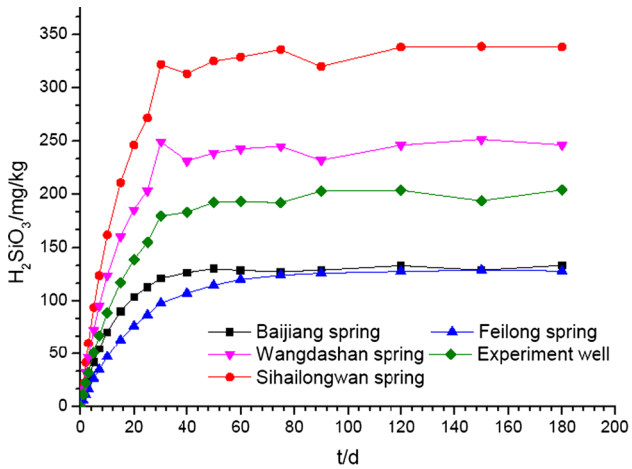

Fig. 7 The curve of H_2SiO_3 of pH acidic experiment

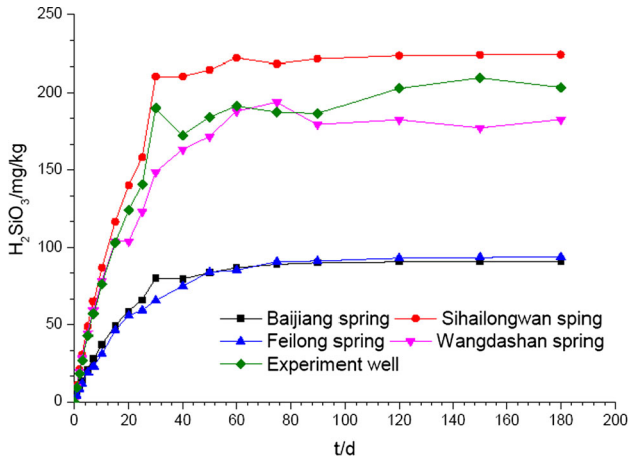

Fig. 8 The curve of H_2SiO_3 of pH alkaline experiment

$$M_t = 241.73 + \frac{-253.71}{1 + \exp\left[(t - 12.449)/3.74\right]} \quad (6)$$

$$M_t = 219.91 + \frac{-225.67}{1 + \exp\left[(t - 10.706)/2.66\right]} \quad (7)$$

$$M_t = 245.3[1 - \exp(-0.12t)]. \quad (8)$$

Table 3 The kinetic model parameters for metasilicate release process in the acidic experiment

Location of rock samples	M_0 (mg/kg)	k_m (d)	Fitting equation	R^2
Baijiang spring	133.18	0.075	$M_t = 133.18[1 - \exp(-0.075t)]$	0.96
Wangdashan spring	246.04	0.07	$M_t = 246.04[1 - \exp(-0.07t)]$	0.97
Feilong spring	128.15	0.045	$M_t = 128.15[1 - \exp(-0.045t)]$	0.991
Sihailongwan spring	338.05	0.065	$M_t = 338.05[1 - \exp(-0.065t)]$	0.95
Experimental well	203.79	0.057	$M_t = 203.79[1 - \exp(-0.057t)]$	0.95

Table 4 The kinetic model parameters for metasilicate release process in the alkaline experiment

Location of rock samples	M_0 (mg/kg)	k_m (d)	Fitting equation	R^2
Baijiang spring	90.75	0.052	$M_t = 90.75[1 - \exp(-0.052t)]$	0.95
Wangdashan spring	182.70	0.056	$M_t = 182.70[1 - \exp(-0.056t)]$	0.96
Feilong spring	93.70	0.04	$M_t = 93.70[1 - \exp(-0.04t)]$	0.96
Sihailongwan spring	224.02	0.049	$M_t = 224.02[1 - \exp(-0.049t)]$	0.98
Experimental well	203.50	0.047	$M_t = 203.50[1 - \exp(-0.047t)]$	0.95

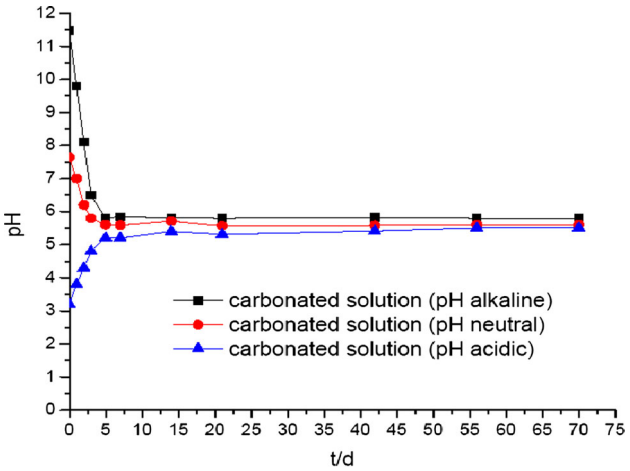

Fig. 9 The curve of pH of carbonated solution experiment

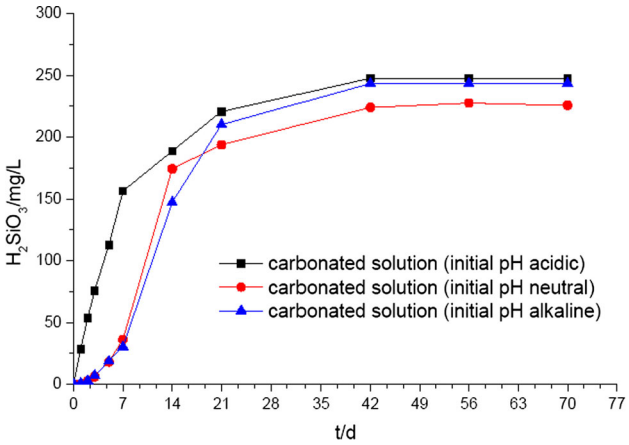

Fig. 10 The curve of $H_2SiO_3^-$ of carbonated solution experiment

Mineral reaction mechanism

Table 5 shows the chemical reactions that may occur in the water soluble experiment and ΔG of the reactions with the constraints was (9). Table 6 shows the ion concentration of the initial solution and balanced solution of the water soluble experiment. Table 7 shows the optimal feasible solution.

$$\begin{cases} X_2 = 0.161 \\ X_4 - X_6 = 0.162 \\ 2X_3 + X_4 - X_5 = 0.11 \\ 3X_7 - X_8 = 0.0023 \\ X_1 + 3X_2 + X_3 + 2X_4 = 0.331 \end{cases} \quad (9)$$

Table 8 shows the physical and chemical reactions that may occur in the alkaline pH experiment and ΔG of the reactions with the constraints was (10). Table 9 shows the ion concentration of the initial solution and balanced solution of the alkaline pH experiment. Table 10 shows the optimal feasible solution.

$$\begin{cases} X_2 = 0.099 \\ X_4 = 0.054 \\ 2X_3 = 0.11 \\ X_5 + X_6 + X_7 = 0.0023 \\ X_1 + 3X_2 + X_3 + 2X_4 = 0.275 \end{cases} \quad (10)$$

Table 11 shows the physical and chemical reactions that may occur in the carbonated solution experiment (initial pH acidic) and ΔG of the reactions with the constraints was

Table 5 The chemical reactions and the free-energy change of water solution experiments at 25 °C

Reactive substance	Chemical reaction	ΔG_r (J/mol)
SiO_2	$SiO_2 + H_2O \rightarrow H_4SiO_4$	−214
$NaAlSi_3O_8$	$NaAlSi_3O_8 + 5.5H_2O \rightarrow Na^+ + 0.5Al_2Si_2O_5(OH)_2 + 3H_4SiO_4 + OH^-$	−1189.03
Mg_2SiO_4	$Mg_2SiO_4 + 4H_2O \rightarrow 2\ Mg^{2+} + 4OH^- + H_4SiO_4$	153.425
$CaMgSi_2O_6$	$CaMgSi_2O_6 + 6H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4OH^- + 2H_2SiO_4$	199.06
Mg^{2+}	$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$	−66.1
Ca^{2+}	$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$	−29.44
Fe_3O_4	$Fe_3O_4 + 8H^+ \rightarrow 3Fe^{3+} + 4H_2O$	32.3
Fe^{3+}	$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$	−214.2

Table 6 The ion concentrations of the initial solution and equilibrium solution for the water solution experiment (mmol/L)

Component	K^+	Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	H_4SiO_4
Initial solution	0	0	0	0	0	0	0	0	0	0
Equilibrium solution	0.0235	0.161	0.162	0.11	0.0023	1.080	0	0	0.0684	0.331
Δm[a]	0.0235	0.161	0.162	0.11	0.0023	1.080	0	0	0.0684	0.331

[a] Δm is the variation in ion concentrations between initial and equilibrium solutions

Table 7 The optimal feasible solution for the water solution experiment

X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
SiO_2	$NaAlSi_3O_8$	Mg_2SiO_4	$CaMgSi_2O_6$	Mg^{2+}	Ca^{2+}	Fe_3O_4	Fe^{3+}
0.0001	0	0	0.0001	0	0	0.3779	1.1338

All values are given in mmol/L

Table 8 The chemical reactions and the free-energy change for the alkaline experiment at 25 °C

Reactive substance	Chemical reaction	ΔG_r (J/mol)
SiO_2	$SiO_2 + H_2O \rightarrow H_2SiO_3$	−164.36
$NaAlSi_3O_8$	$NaAlSi_3O_8 + 2H_2O + 6OH^- \rightarrow Na^+ + Al(OH)_4^- + 3H_2SiO_4^{2-}$	−613.55
Mg_2SiO_4	$Mg_2SiO_4 + 4H_2O \rightarrow 2\ Mg(OH)_2 + H_4SiO_4$	21.225
$CaMgSi_2O_6$	$CaMgSi_2O_6 + 6H_2O \rightarrow Ca(OH)_2 + Mg(OH)_2 + 2H_4SiO_4$	103.518
$Mg(OH)_2$	$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$	66.1
$Ca(OH)_2$	$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$	29.442
Fe_3O_4	$Fe_3O_4 + 4H_2O \rightarrow Fe(OH)_2 + 2Fe(OH)_3$	−630
$Fe(OH)_2$	$Fe(OH)_2 \rightarrow Fe^{2+} + 2OH^-$	−66.7
$Fe(OH)_3$	$Fe(OH)_3 \rightarrow Fe^{3+} + 3OH^-$	−25.5

(11). Table 12 shows the ion concentration of the initial solution and balanced solution of the carbonated solution experiment (initial pH acidic). Table 13 shows the optimal feasible solution.

$$\begin{cases} X_2 = 0.097 \\ X_3 - X_6 = 1.458 \\ 2X_1 + X_3 = 1.518 \\ 3X_7 = 0.00947 \\ 4X_1 + X_2 + 4X_3 - X_5 = 3.241 \\ X_1 + 2X_2 + 2X_3 + X_4 = 0.390 \end{cases} \quad (11)$$

Discussions

The pH of the solution, catalyst, samples state generally have the great impact on chemical reaction (Christoskova and Stoyanova 2009), and when varying these factors our experimental results showed different magnitudes for metasilicate release. In the water soluble experiment, the pH of the reaction solution increased to weakly alkaline because the basalt rock samples were alkaline (Chen and Zhang 1994). In the alkaline solution, H_2O and OH^-

Table 9 The ion concentrations of the initial solution and equilibrium solution for the alkaline experiment (mmol/L)

Component	K^+	Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	H_4SiO_4
Initial solution	0	0	0	0	0	0	0	0	0	0
Equilibrium solution	0.0165	0.099	0.054	0.11	0.0023	1.945	0	0	0.1368	0.275
Δm[a]	0.0165	0.099	0.054	0.11	0.0023	1.945	0	0	0.1368	0.275

[a] Δm is the variation in ion concentrations between initial and equilibrium solutions

Table 10 The optimal feasible solution for the alkaline experiment

X_1	X_2	X_3	X_4	X_5	X_6	X_7
SiO_2	$NaAlSi_3O_8$	Mg_2SiO_4	$CaMgSi_2O_6$	Fe_3O_4	$Fe(OH)_2$	$Fe(OH)_3$
0.01	0.099	0.055	0.054	0.5029	0.0002	0.0532

All values are given in mmol/L

Table 11 The chemical reactions and the free-energy change for the carbonated solution experiment (initial pH acidic) at 25 °C

Reactive substance	Chemical reaction	ΔG_r (J/mol)
Mg_2SiO_4	$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2\ Mg^{2+} + 4HCO_3^- + H_4SiO_4$	−322.975
$NaAlSi_3O_8$	$NaAlSi_3O_8 + CO_2 + 5.5H_2O \rightarrow 0.5Al_2Si_2O_5(OH)_4 + Na^+ + 2H_4SiO_4 + HCO_3^-$	81.87
$CaMgSi_2O_6$	$CaMgSi_2O_6 + 4CO_2 + 6H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- + 2H_2SiO_4$	51.06
SiO_2	$SiO_2 + H_2O \rightarrow H_4SiO_4$	−214
HCO_3^-	$HCO_3^- \rightarrow H^+ + CO_3^{2-}$	58.9
Ca^{2+}	$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$	−47.36
Fe_3O_4	$Fe_3O_4 + 8H^+ \rightarrow 3Fe^{3+} + 4H_2O$	32.3

Table 12 The ion concentrations of the initial solution and equilibrium solution (mmol/L)

Component	K^+	Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	HCO_3^-	SO_4^{2-}	Cl^-	F^-	H_4SiO_4
Initial solution	0	0	0	0	0	0	0	0	0	0
Equilibrium solution	0.0208	0.097	1.458	1.518	0.00947	3.241	0.218	2.377	0.0156	0.390
Δm[a]	0.0208	0.097	1.458	1.518	0.00947	3.241	0.218	2.377	0.0156	0.390

[a] Δm is the variation in ion concentrations between initial and equilibrium solutions

provide a strong base, while strongly acidic mineral elements are also present in basalt, such as Al^{3+}, based on Pearson's hard and soft acid–base theory (HSAB) (Pearson 1963). H_2O and OH^- combined with metal cation with basalt sample forming hydrolyzate or hydroxide, and SiO_2 combined with alkali forming silicate and metasilicate according to the "hard pro hard" law (Wisniewski 2006). Plagioclase, olivine, and pyroxene reacted with H_2O-generated silicate and metasilicate, but also produced precipitates that hinder the reaction's progress by covering the mineral surface. In the acidic solution, the dissolution reaction of silicate minerals can be summarized by Eq. 12, and the rate of the dissolution reaction of silicate minerals increases with the concentration of H^+ (Helgeson 1970; Yu 1994).

$$M(\text{mineral}) + \text{n}H^+ \longrightarrow SiO_2 + Al_2O_3 + M_0^{\text{n}+}. \quad (12)$$

In deionized water with neutral pH, the solubility of the silicate mineral is extremely low, but with the addition of the catalyst (CO_2), a large amount of H^+ is produced by CO_2 and H_2O, making the reaction solution acidic. Thus, in the carbonated solution experiments with an initially neutral or alkaline pH, a change was found after 7 days when the pH of reaction solution reduced to acidic.

In the water soluble experiment, the release process of metasilicate for the powdered sample matched the Stanford

Table 13 The optimal feasible solution for the carbonated solution experiment (initial pH acidic)

X_1	X_2	X_3	X_4	X_5	X_6	X_7
Mg_2SiO_4	$NaAlSi_3O_8$	$CaMgSi_2O_6$	SiO_2	HCO_3^-	Ca^{2+}	Fe_3O_4
2.0743	0.0970	1.4381	1.4066	0	0	0.0032

All values are given in mmol/L

reaction kinetic model, while the process of metasilicate release for the solid sample followed an asymptotic model. In the powdered sample experiments, rock particles and the reaction solution have full contact, leading to an increased reaction rate and to the reaction reaching equilibrium faster. In the acidic–alkaline experiment, the release process of metasilicate for the powdered samples all matched the Stanford reaction kinetic model, but the reaction mechanisms differed. For alkaline experiments ($7.00 < pH < 10.61$), metasilicate formation is produced by the hydrolysis of SiO_2, plagioclase, olivine, and pyroxene, but the secondary minerals also inhibit the reaction by covering the surface of the rock samples. For acidic ($2.46 < pH < 7.00$) experiments, metasilicate formation is predominantly from the reaction of H^+ and SiO_2, plagioclase, olivine, and pyroxene. The addition of CO_2 can adjust the pH of the solution (Aiman and Al 2010). In the carbonated solution experiment, the release process of metasilicate with the initially neutral or alkaline solutions complied with the Boltzmann reaction kinetic model, while initially acidic solutions complied with the Stanford reaction kinetic model. For the carbonated experiment, metasilicate formation is mainly from the reaction of CO_2 and H_2O, plagioclase, olivine, and pyroxene. Since CO_2 reacted as an aqueous solution, its products were H_2CO_3 with a neutral or alkaline pH, meaning the rate of metasilicate release is relatively small initially, until the pH of the reaction solution becomes acidic.

The pH value of precipitation of Jingyu was faintly acid. Rainfall infiltrated into groundwater through humus layer, causing pH of groundwater to reduce. In the exposed bedrock area, the pH of groundwater was found to be alkaline. So the metasilicate mineral water of Jingyu was generated by the hydrolysis of metasilicate mineral and the reaction of H^+, CO_2, and metasilicate mineral together.

Conclusions

The study presents the impact of the pH and CO_2 on the formation of Metasilicate mineral water in Changbai Mountain, Northeast China by experimental methods, chemical kinetic analysis, and minimum free-energy method. The general conclusions can be drawn from this study.

(1) The laws of the metasilicate release process all increased firstly and then reached equilibrium state. pH values of the reaction solutions become essentially neutral.
(2) The release process of metasilicate of solid rocks was slower than that of powdered rocks in the same experimental conditions; and the release process of metasilicate of solid rocks satisfied asymptotic model while that of powdered rocks fit in with Stanford reaction kinetic model.
(3) It was earlier to forming metasilicate in the condition of acidic pH ($2.46 < pH < 7.00$) than in the condition of alkaline pH ($7.00 < pH < 10.61$), as the release process of metasilicate fits in with Stanford reaction kinetic model. Addition of CO_2 was beneficial to the formation of metasilicate, and the release process of metasilciate accorded with Boltzmann equation in the condition of neutral and alkaline pH.
(4) In the condition of neutral pH, metasilicate formation was mainly from the hydrolysis of SiO_2, but the reaction was difficult. In the condition of alkaline pH ($7.00 < pH < 10.61$), metasilicate formation was produced from the hydrolysis of SiO_2, Plagioclase, Olivine, and Pyroxene; but the secondary mineral also inhibit the reaction covering the surface of rock samples. In the condition of acidic pH ($2.46 < pH < 7.00$), metasilicate formation was mainly from the reaction of H^+ and SiO_2, Plagioclase, Olivine, and Pyroxene. In the condition of CO_2 catalytic, metasilicate formation was mainly from the reaction of CO_2, H_2O, Plagioclase, Olivine, and Pyroxene.
(5) The metasilicate mineral water of Jingyu was generated by the hydrolysis of metasilicate mineral and the reaction of H^+, CO_2, and metasilicate mineral together.

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